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(54) Hot-stamping glass.

(57) A method for applying decorative coating to glass which comprises the steps of:

- 3) applying a pattern of decoration to the glass with a curable adhesive ink,
- b) curing the adhesive ink,
- c) compressing a foil bearing a film of decorative material against the glass with a compress heated to at least 395K (250 °F), and
- d) after removal of the compress peeling off the foil whereby the decorative film thereon remains adhered to the adhesive ink pattern only.

Further an adhesive ink is disclosed comprising a monomer, a polymer dissolved in said monomer, and a polymerisation-initiating agent, preferably a photo-initiator.

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This invention relates to the application of decorative coatings to glass, by a procedure akin to that known as hot-stamping.

The known hot-stamping procedure involves using a heated die or roller to apply both heat and pressure to a so-called foil, consisting of a pigmented color or metallized surface film borne on an usually-polyester carrier, so as to force it into contact with thermoplastic substrate, and thereby soften the thermoplastic substrate and also activate the film-coating on the foil, thereby enabling it to form a strong physico-chemical bond with the underlying thermoplastic substrate wherever heat and pressure have been applied to the foil, but not elsewhere. When subsequently the foil is pulled away, just the areas of the film which have been subjected to the hot-stamping remain affixed to the plastic substrate, and the remainder peels away. In order to carry out this operation one normally employs either a vertical stamping or a roll-on machine. The vertical stamping machine contains a heated die of brass, steel or silicone rubber, which serves to apply both heat and pressure and thus to transfer the desired pattern (whatever that may be - thus decorative areas and/or writing or other printed information) of the film on to the plastic substrate, as each part is positioned beneath the die. Roll-on methods utilize a silicone rubber roller or an arcuate die to transfer the desired pattern from the foil on the thermoplastic substrate in either a continuous or a batch process.

Hot-stamping is an efficient and inexpensive way to apply decoration to thermoplastic substrates. Unfortunately however hot-stamping of this nature cannot be used with glass, because glass melts at a much higher temperature than most thermoplastic materials. Consequently decoration in the form of gold leaf, color design or printing etc. is generally applied to glass containers by a glazing process similar to that used with ceramics. Thus for example in gold-leafing the gold decoration is applied to the glass container by a variety of methods such as or akin to silk screen printing, etc. The glass container is then subjected to extremely high kiln temperatures, and in essence the decoration is baked on. Unfortunately this process is however time-consuming, expensive, energy-intensive and gives rise to safety considerations due to the high temperatures that have to be employed and the nature of the gases which are involved in the operation of the kilns.

There is thus a great need for a simple, economical and ultra-safe procedure for applying decoration to glass substrates, and we have devised a method for achieving this objective which is akin to the known hot-stamping process but operable on glass.

According to this invention there is provided a method for applying a decorative coating to glass, which comprises the steps of:

- a) applying a pattern of decoration to the glass with a curable adhesive ink;
- b) curing the adhesive ink;
- c) compressing a foil bearing a film of decorative material against the glass with a compress heated to at least 395K (250°F); and
- d) after removal of the compress peeling off the foil whereby the decorative film thereon remains adhered to the adhesive ink pattern only.

According to another aspect of the invention there is also provided an adhesive ink composition for use in the method herein disclosed, which adhesive ink comprises a monomer, a polymer dissolved in the monomer, and a polymerization-initiating agent.

A wide variety of glass containers may be provided with a decorative coating by means of the method of this invention, including for instance bottles, dishes, cups and glasses - and so far as we are aware there is no limit on the kind of glass that may thus be decorated.

In the first step, the desired decorative or other pattern is essentially "painted" onto the glass utilizing an adhesive ink as the "paint". The "painting" may be accomplished by silk screening, stenciling, actual painting or any other of the wide variety of available methods. We currently prefer to apply the desired pattern of adhesive ink by silk-screening it onto the glass container, utilizing the traditional screen and squeegee well known to those skilled in the art.

The adhesive ink employed in the method must be a curable polymeric composition, and we believe that it should very desirably contain at least a monomer, a polymer dissolved in the monomer, and a polymerization-initiating agent. The adhesive ink may however advantageously also contain other useful ingredients, e.g. silanes may be included to improve adhesion.

Suitable monomers include isobornyl acrylate, urethane methacrylate, urethane acrylate, tetrahydrofurfuryl acrylate, acrylic resins, aromatic urethane acrylic resin, etc.

A wide variety of polymers can be utilized, including for instance polythylmethacrylate, polymethylmethacrylate, polyurethane, polyester acrylates, epoxy acrylates, etc.

Equally, a wide variety of polymerization-initiators may be utilized, including initiators activated by heat, by various chemicals or by actinic radiation, often in the ultraviolet spectrum.

Photo-initiators suitable for use with actinic radiation include 1-hydroxycyclohexylphenylketone, 2,2-dimethoxy-2-phenyl acetophenone, diethoxyacetophenone and 2-methyl-1-(methylethiophenyl)-2-(4-morpholinyl)-1-propanone.

In our preferred procedure the monomer is isobornyl acrylate or urethane methacrylate, and/or the preferred polymer is polyethylmethacrylate, and/or the preferred photo-initiator is 1-hydroxycyclohexylphenylketone - the latter being marketed under the tradename Irgacure 184 (Ciba-Geigy, Hawthorne, NY).

It is desirable to include a silane, specifically 3-glycidioxy-propyl trimethyl silane, in the adhesive ink. Silane is a known coupling agent with glass, and will increase bond strength.

Generally the monomer concentration will be in the range of from 20 to 90%; the polymer concentration will be in the range of from 10 to 35%; and the photo-initiator concentration will be in the range of from about 3 to 10%. If silane is added to the composition, we recommend the use of from about 1 to 10%.

Other ancillary ingredients may be added to the composition for particular purposes, e.g. to enhance adhesion and/or to improve the cure rate and/or for other reasons, such as acrylic acid derivatives, stabilizers, inert fillers and so on.

It can for some purposes be advantageous to include pigments in the adhesive ink. The pigmented ink may still be silk screened or painted onto the glass container and cured as usual. The inclusion of pigment in the adhesive ink has certain advantages - firstly that it renders the adhesive ink more readily visible after application to the glass, and secondly that the use of pigmented ink in conjunction with the use of foil can enable one to provide a two-tone effect. Suitably-colored pigmented adhesive inks can be made by simply adding an appropriate amount e.g. from 1 to 20%, of the chosen pigment to the adhesive ink composition. Thus for instance colored adhesive inks can be made by adding say 10% of titanium dioxide to the composition so as to color it white, or by adding say 15% of carbon black to the composition so as to color it black.

As mentioned previously, the adhesive ink must be cured in situ, after it has been applied to the glass substrate. Curing is effected in whatever manner is appropriate. This will usually be dependent on the type of polymerization-initiator used. If one uses radiation-sensitive photo-initiators which are sensitive to actinic radiation, then the adhesive may readily be cured by passing the decorated container under the appropriate intensity of ultraviolet light. We currently prefer to employ an adhesive ink which is curable by actinic radiation, so the containers can be passed under ultraviolet light using a conventional UV conveyor.

After the desired pattern of adhesive ink on the container has been cured, then the foil bearing the film of the desired gold, silver or other decorative material is compressed against the container by means of a stamp, roller or any other suitable compress. The stamp must be heated to a temperature of at least 395K (250°F), and it must also be compressed tightly against the foil-covered glass container. It is possible for this purpose to use a hand-held heated roller such as those made by Silicon Limited, Lancaster, New York State, United States of America.

The roller or stamp should be used to compress the foil against the container for such period as is necessary, but we have found that a period of from 1 to 3 seconds will usually suffice.

When the roller is removed and the foil is peeled away, the film adheres only to the portion of the container decorated with the adhesive ink.

As will be seen, the method of providing a foil decoration on glass substrates according to this invention is simply and inexpensive, above all because it eliminates the need to employ high-temperature kilns and the like to accomplish decorative designs on glass containers.

According to another aspect of this invention we also provide glass substrates decorated by the methods herein disclosed.

In order that the invention may be well understood it will now be further described in more detail, though only by way of illustration with reference to the following examples:

Example 1: Preparation of UV-curable adhesive ink, and subsequent hot-stamping of glass containers therewith

37.5 Grams of isobornyl acrylate (Borden Chemical Co., Cincinnati, Ohio, United States of America) and 12.5 grams of Elvacite 2-13 (DuPont Co., Wilmington, Delaware, United States of America) were mixed together and warmed in a microwave oven for one minute (or if necessary longer) until the Elvacite was completely dissolved in the isobornyl acrylate. 2.5 Grams of a photo-initiator known as Irgacure 184 were then added and mixed in until dissolved.

The adhesive ink obtained as described above was used to silk-screen designs onto a glass container. The screen consisted of a 255 line (39.8 fibers/cm² = 255 fibers/square inch) screen, with the desired decorative design imprinted on it. The imprinted screen was brushed over with a squeegee, resulting in a

glass container with the desired pattern of ink decoration thereon.

The adhesive ink was cured utilizing a 300 watt 0.152 cm^{-1} (30 feet/minute) UV conveyor. The glass container was passed through the conveyor from one to three times, so as to achieve an appropriate degree of curing of the polymer.

5 Gold-colored hot-stamping foil (Crown, Royal Leaf, Paterson, New Jersey, United States of America) was then compressed against the container, utilizing a heated hand-held roller (Silicon Limited, Lancaster, New York State, United States of America). The heated roller was applied for a few seconds, and then the foil was peeled away. The decorative film on the foil adhered only to the previously-formed pattern of adhesive ink.

10 In this manner an excellent, smooth-surfaced decoration with no irregularities was successfully applied to the glass container.

Example 2: Preparation of UV-curable adhesive ink

15 An adhesive composition was formulated as follows:

20	Aromatic urethane methacrylate (Ebecryl 6700, RadCure Specialities, Atlanta, Georgia, U.S.A.)	55 grams
	Tetrahydrofurfuryl acrylate (Sartomer 203, Exton, Pennsylvania, U.S.A.)	20 grams
	Isobornyl acrylate (Sartomer 506, Exton &c)	20 grams
	Defoaming agent (BYK-052, Ciba-Geigy, Hawthorne, New York State, U.S.A.)	0.5 grams
25	Photo-initiator (Irgacure 184)	5 grams
		<u>100.5 grams</u>

The ingredients of this composition were mixed together in the same manner as set forth in Example 1, to form an adhesive ink. The adhesive ink formulation was then transferred in a desired pattern onto a glass slide, utilizing a silk-screening method. The adhesive ink was then cured, utilizing a UV conveyor with a 300 watt lamp and a speed of 0.152 ms^{-1} (30 feet/minute); and it was found that four passes through this UV conveyor were needed fully to cure the adhesive ink.

The formulation was smooth and the cure time acceptable, but adherence of the gold foil after the hot-stamping process was spotty.

35 Example 3: Preparation of adhesive ink

A UV curable adhesive ink composition was formulated as follows:

40	Isobornyl acrylate (Sartomer 203)	24 grams
	Urethane acrylate (Sartomer 9625)	17 grams
	Aromatic urethane acrylate (Ebecryl A 827, RadCure)	5 grams
	Aromatic urethane acrylate (Ebecryl 6700, Radcure)	11 grams
45	Photo-initiator (Irgacure 184)	2.5 grams
	Wetting agent (BYK-501, Union Carbide)	0.5 grams
	Wetting agent (FC 171, Union Carbide)	0.5 grams
	Levelling agent (A 151, Union Carbide)	0.5 grams
50		<u>61 grams</u>

The adhesive ink thus formulated was transferred onto a glass container in the desired pattern using a silk-screening process. The ink thus applied was smooth, provided a surface without irregularities, and adhered well to the glass.

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Example 4: Preparation of adhesive ink

An adhesive ink composition was formulated as follows:

5	Loctite 36331 (Loctite Corp., Newington, Connecticut, U.S.A.)	75 grams
	Polymethylmethacrylate (Elvacite 2043, DuPont Corp., Wilmington, Delaware, U.S.A.)	25 grams
	Photo-initiator (Irgacure 184)	2 grams
		<u>102 grams</u>

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This composition was mixed for about one hour in a mixer. The ink was then transferred in the desired pattern by silk-screening, using a 255 line screen, onto a glass container. The adhesive was cured by four passes through a 300 watt 0.152 ms^{-1} (30 feet/minute) UV conveyer.

The surface was a bit bumpy and uneven after hot-stamping.

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Example 5: Preparation of adhesive ink

An adhesive ink composition was formulated as follows:

20	Urethane methacrylate	27 parts
	High boiling methacrylate resin	55 parts
	Acrylic acid	5 parts
	Hydroxyethylmethacrylate	5 parts
25	Photo-initiator	5 parts
	Substituted silane (Dow Corning, Huls Silane Ester "Scatterway")	3 parts

The resulting formulation provides an excellent, easily-curable adhesive ink which works well with hot-stamping.

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Claims

1. A method for applying decorative coating to glass which comprises the steps of:
 - a) applying a pattern of decoration to the glass with a curable adhesive ink,
 - b) curing the adhesive ink,
 - c) compressing a foil bearing a film of decorative material against the glass with a compress heated to at least 395K (250°F), and
 - d) after removal of the compress peeling off the foil whereby the decorative film thereon remains adhered to the adhesive ink pattern only.
2. A method as claimed in claim 1, in which the adhesive ink is cured by heat and/or by a polymerization-initiating agent.
3. A method as claimed in claim 2 in which the polymerization-initiating agent is or includes a chemical cross-linked and/or actinic radiation.
4. A method as claimed in any of the preceding claims, in which the curable adhesive ink comprises a monomer, a polymer dissolved in the monomer, and a polymerization-initiating agent.
5. A method as claimed in claim 4, in which the polymerization-initiating agent is or includes a photo-initiator.
6. A method as claimed in claim 5, in which the photo-initiator is 1-hydroxyhydrocyclohexylphenylketone.
7. A method as claimed in any of the preceding claims, in which the pattern of decoration in curable adhesive ink is applied by a silk-screening process.
8. A method as claimed in any of the preceding claims, in which the compress employed is a roller.

9. A method as claimed in any of the preceding claims, in which the glass is in the form of a bottle.
10. A method as claimed in claim 9, in which the glass takes the form of a nail-enamel bottle.
- 5 11. A method as claimed in any of claims 4 to 10, in which the adhesive ink composition comprises:
 - a) from 20 to 90% of the monomer;
 - b) from 10 to 35% of the polymer dissolved in the monomer; and
 - c) from 3 to 10% of the photo-initiator;all these percentages being by weight of the total composition.
- 10 12. A method as claimed in any of claims 4 to 11, in which the monomer is or includes isobornyl acrylate, urethane methacrylate, urethane acrylate, tetrahydrofurfuryl acrylate, acrylic resins and/or aromatic urethane acrylic resin.
- 15 13. A method as claimed in any of claims 4 to 11, in which the monomer is or includes isobornyl acrylate and/or urethane methacrylate.
14. A method as claimed in any of claims 4 to 13, in which the polymer is or includes polyethylmethacrylate, polymethylmethacrylate, polyurethane, polyester acrylates and/or epoxy acrylates.
- 20 15. A method as claimed in any of claims 4 to 13, in which the polymer is or includes polyethylmethacrylate.
- 25 16. A method as claimed in any of claims 4 to 15, in which the photo-initiator is or includes 1-hydroxycyclohexylphenylketone, 2,2-dimethoxy-2-phenylacetophenone, diethoxyacetophenone and/or 2-methyl-1-(methylethiophenyl)-2-(4-morpholinyl)-1-propanone.
17. A method as claimed in any of claims 4 to 15, in which the photo-initiator is or includes 1-hydroxycyclohexylphenylketone.
- 30 18. A method as claimed in any of the preceding claims, in which the adhesive ink composition additionally comprises, by weight of the total composition, from 1 to 10% of silane.
19. A method as claimed in claim 18, in which the silane is or includes 3-glycidioxy-propyl trimethyl silane.
- 35 20. A method as claimed in any of the preceding claims, in which the composition additionally comprises, by weight of the total composition from 1 to 20% of pigment.
- 40 21. An adhesive ink composition, for use in the method claimed in any of the preceding claims, which adhesive ink comprises a monomer, a polymer dissolved in the monomer, and a polymerization-initiating agent.
22. A composition as claimed in claim 21, in which the polymerization-initiating agent is or includes a photo-initiator.
- 45 23. A composition as claimed in claim 22, in which the photo-initiator is 1-hydroxyhydrocyclohexylphenylketone.
24. A composition as claimed in any of claims 21 to 23, which comprises:
 - 50 a) from 20 to 90% of the monomer;
 - b) from 10 to 35% of the polymer dissolved in the monomer; and
 - c) from 3 to 10% of the photo-initiator;all these percentages being by weight of the total composition.
- 55 25. A composition as claimed in any of claims 21 to 24, in which the monomer is or includes isobornyl acrylate, urethane methacrylate, urethane acrylate, tetrahydrofurfuryl acrylate, acrylic resins and/or aromatic urethane acrylic resin.

26. A composition as claimed in any of claims 21 to 25, in which the polymer is or includes polyethylmethacrylate, polymethylmethacrylate, polyurethane, polyester acrylates and/or epoxy acrylates.
27. A composition as claimed in any of claims 21 to 25, in which the photo-initiator is or includes 1-hydroxycyclohexylphenylketone, 2,2-dimethoxy-2-phenylacetophenone, diethoxyacetophenone and/or 2-methyl-1-(methylethiophenyl)-2-(4-morpholinyl)-1-propanone.
28. A composition as claimed in any of claims 21 to 27, additionally comprises, by weight of the total composition, from 1 to 10% of silane.
29. A composition as claimed in claims 21 to 28, in which the silane is or includes 3-glycidoxy-propyl trimethyl silane.
30. A composition as claimed in any of claims 21 to 29, which additionally comprises, by weight of the total composition, from 1 to 20% of pigment.



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EUROPEAN SEARCH REPORT

Application Number

EP 93 30 4160

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	DATABASE WPI Section Ch, Week 8448, Derwent Publications Ltd., London, GB; Class L, AN 84-297751 & JP-A-59 184 746 (KOA GLASS KK) 20 October 1984 * abstract * ---	1-3,8-10	C 03 C 17/38 B 44 C 1/14 C 09 D 11/10
Y	---	11-20,4-7	
X	PATENT ABSTRACTS OF JAPAN vol. 6, no. 260 (M-180)18 December 1982 & JP-A-57 152 992 (KAMAYA KAGAKU KOGYO KK) 21 September 1982 * abstract * ---	1-3,8-10	
Y	---	11-20,4-7	
Y	EP-A-0 106 628 (JOHNSON MATTHEY PUBLIC LIMITED COMPANY) * page 9, last paragraph - page 10; claims 1,4,5,7-9; page 14, last paragraph - page 15, paragraph 1 * ---	4-7,11-20	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
Y	PATENT ABSTRACTS OF JAPAN vol. 14, no. 90 (C-691)(4033) 20 February 1990 & JP-A-13 001 535 (HAYAKAWA RUBBER CO LTD) 5 December 1989 * abstract * ---	4-7,11-20	C 03 C B 44 C C 09 D
A	RESEARCH DISCLOSURE no. 328, August 1991, EMSWORTH GB page 618 'Photoinitiator Combinations for UV Curable Screen Printing Inks' * the whole document * --- -/-	6,17	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 27-12-1993	Examiner VAN BOMMEL L
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons Δ : member of the same patent family, corresponding document			



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CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

- ☐ All claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for all claims.
- ☐ Only part of the claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid, namely claims:
- ☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirement of unity of invention and relates to several inventions or groups of inventions, namely:

See sheet -B-

- ☐ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.
- ☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:
- ☒ None of the further search fees has been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims: 1-20



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EUROPEAN SEARCH REPORT

Application Number

EP 93 30 4160

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CL.5)
X	CHEMICAL ABSTRACTS, vol. 93, no. 24, 15 December 1980, Columbus, Ohio, US; abstract no. 224638x, page 253 ; & JP-A-55023222 * abstract * ---	1,2,8-10	
X	PATENT ABSTRACTS OF JAPAN vol. 12, no. 218 (M-711)22 June 1988 & JP-A-63 017 075 (HINO JUSHI KK) 25 January 1988 * abstract * -----	1,2,7,8	
			TECHNICAL FIELDS SEARCHED (Int. CL.5)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 27-12-1993	Examiner VAN BOMMEL L
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : oral-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document	